

SCALE INHIBITION IN WATER SYSTEMS

This invention relates to scale inhibition in water systems.

In particular, the present invention relates to use of a composition for inhibiting the formation of scale (especially barium sulphate scale) in water systems (especially systems where the fluids are exposed to a range of temperatures, e.g. in hydrocarbon production, where temperatures are high at a sub-sea wellhead and reduce as the fluids travel to the production facility along a sub-sea tie-line). Conventionally, scale inhibitors tend to function well either at high or low temperatures, but not both.

We also claim methods for inhibiting the formation of scale in water systems by means of such compositions and to water systems so treated.

At the wellhead, fluids can often be at 100°C or more whereas, along the tie-line, the temperature can reduce to as little as 5°C before the fluids reach the production facility.

It is therefore vital to ensure that effective scale control is provided over the whole temperature range to which the fluids are exposed, particularly for sub-sea wells (including deepwater applications) with long tie-backs. Here, produced fluids typically travel around many tens of km along the sea-bed and in such applications, the costs of intervention, should scale occur, are high.

Previous technology has involved the use of scale inhibitors, such as phosphonates (which are maximally effective at high temperatures) and sulphonated polymers (which are maximally effective at low temperatures) but, hitherto, scale inhibitors which are fully effective at both low and high temperatures have not been available.

The present invention also relates to use of compositions to control scale deposition in systems operating under highly alkaline conditions. Such conditions are found in a variety of industrial applications, such as mineral ore extraction (e.g. heap leach processes), drilling and fracturing fluids, highly cycled process waters, alkaline bleaching systems, bottle washing systems, industrial cleaning processes, chemical pulping of wood, Kraft digesters, black liquor digesters, lime kiln gas scrubbers, evaporators, desalination systems, boiler water, cooling waters, reverse osmosis systems, etc. We also claim methods of controlling scale deposition in systems operating under highly alkaline conditions and water systems so treated.

We have now unexpectedly found that copolymers or terpolymers containing both phosphonate and sulphonate groups (with the addition in terpolymers, of carboxylate groups) can produce enhanced scale-inhibition in water systems over a range of temperatures. These copolymers and terpolymers can also provide scale formation control in systems operating under highly alkaline conditions.

In a first aspect, therefore, the present invention provides the use of a composition in a water system to inhibit the formation of scale at high (e.g. wellhead) and low (e.g. seabed) temperatures wherein the composition comprises:

- (a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) or an unsaturated carboxylic acid (or salt of such an acid)
- or
- (b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) and an unsaturated carboxylic acid (or salt of such an acid).

In particular, the scale is barium sulphate scale.

In a second aspect the present invention provides the use of a composition in a water system operating under highly alkaline conditions to control the deposition of scale wherein the composition comprises:

(a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) or an unsaturated carboxylic acid (or salt of such an acid)

or

(b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) and an unsaturated carboxylic acid (or salt of such an acid).

Examples of suitable unsaturated phosphonic acids include vinylphosphonic acid (VPA) (or a salt thereof) and vinylidene-1,1-diphosphonic acid (VDPA) (or a salt thereof).

Examples of suitable unsaturated sulphonic acids include vinylsulphonic acid (VSA) (or a salt thereof), and AMPS(2-acrylamido-2-methylpropane sulphonic acid) (or a salt thereof) .

Examples of suitable unsaturated carboxylic acids include acrylic acid (AA) (or a salt thereof) and methacrylic acid (MAA) (or a salt thereof).

Accordingly, the composition used in the first aspect and the second aspect of the present invention may comprise any of the following:

- (i) a copolymer of VPA (or a salt thereof) and VSA (or a salt thereof), an especially-preferred copolymer being a 1:5 to 1:40, preferably 1:20, copolymer of VPA and VSA;

- (ii) a copolymer of VPA (or salt thereof) and AA or MAA (or salt thereof)
- (iii) a copolymer of VDPA (or a salt thereof) and AA (or a salt thereof) or MAA (or a salt thereof);
- (iv) a copolymer of VDPA (or a salt thereof) and VSA (or a salt thereof)
- (v) a terpolymer of VPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof);
- (vi) a terpolymer of VPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof);
- (vii) a terpolymer of VDPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof);
- (viii) a terpolymer of VDPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof).

Where a salt of an unsaturated phosphonic, sulphonic or carboxylic acid is used, the salt may be a wholly-neutralised or partially-neutralised salt (for example a wholly- or partially-neutralised sodium, potassium or ammonium salt of the unsaturated acid).

In a third aspect, the present invention provides a method for inhibiting the formation of scale in a water system operating at high (e.g. wellhead) and low (e.g. seabed) temperatures, the method comprising the addition to the water system of a scale inhibiting amount of a composition described in the first aspect of the present invention hereinabove described.

Suitably, the composition is added to the water system in an amount of up to 1000 ppm, more typically 1- 200 ppm.

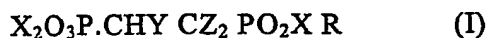
Generally, for sub-sea applications, the seabed temperature of the water system can be as low as 5 degrees Celsius and the wellhead temperature can be up to 200 degrees Celsius.

In a fourth aspect, the present invention provides a method for controlling the deposition of scale, preferably inhibiting the formation of scale, in a water system operating under highly alkaline conditions, the method comprising the addition to the water system of a scale deposition controlling, preferably scale inhibiting, amount of a composition as described in the second aspect of the present invention hereinabove described.

In a fifth aspect, the present invention provides a water system treated by the method according to the third or fourth aspect of the present invention hereinabove described.

Suitably, the water system so treated by a method according to the third aspect is operatively associated with an oilfield or an oil-well. Application may be by injection of the scale inhibitor into the fluid stream by means of, e.g. a dosing pump but often, application is by "squeeze" treatment whereby the scale inhibitor is forced into the oil bearing formation from whence, subsequently, it bleeds back slowly into the produced fluids thus treating them at the appropriate level to inhibit scale.

In a sixth aspect, the present invention provides use in a water system of a composition to control the deposition, preferably inhibit the formation, of scale under highly alkaline conditions wherein the composition comprises a compound of the formula:



where X is H or an alkali metal, alkaline earth or other polyvalent metal, ammonium or an organic base, and R is hydrogen, an alkyl moiety or a group, or polymeric chain comprising between 1 and 100,000 groups, said group or groups being derived from at least one unsaturated compound in which the multiple bond is activated chemically by an adjacent electron withdrawing group, and Y and Z are each hydrogen, a PO_3X_2 , SO_3X or CO_2X group or an alkyl or aryl moiety.

The compounds may exist either as free acids or as their salts. They are normally prepared and used in the form of water soluble salts (e.g. alkali metal salts, especially sodium or potassium salts, or ammonium salts). References herein to the products or their precursors as acids should be construed as including references to the soluble salts where the context permits.

In formula I it may be that X is H or an alkali metal or ammonia, Y is H, each Z is H, and R is H. Alternatively it may be that X is H or an alkali metal or ammonia, Y is X_2O_3P- , each Z is H and R is H. As further alternative it may be that X is H or an alkali metal or ammonia, Y is H or X_2O_3P- , each Z is H and R is $-CH_2CHYPO_3X_2$.

The compound of formula (I) may be a telomer wherein R is a polymeric or copolymeric group formed from at least one monomer selected from unsaturated sulphonic acids, phosphonic acids, carboxylic acids and their water soluble salts.

Preferably the monomer comprises vinyl sulphonic acid and/or its water soluble salt, vinyl phosphonic acid and/or its water soluble salts, vinylidene diphosphonic acid and/or its water soluble salts or acrylic acid.

The monomer may comprise at least one member selected from methacrylic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, vinyl alcohol, vinyl chloride, vinyl acetate, styrene sulphonic acid, 2-acrylamido-2 methylpropane sulphonic acid and their water soluble salts.

The details of manufacture of the compound of Formula (I) are found in European Patent No 0 861 846 of the applicant.

The invention will be illustrated, in a preferred embodiment, by way of the following Examples.

EXAMPLE 1

Methodology

A standard static beaker barium sulphate bottle test used in the industry was followed.

Tested inhibitors are detailed in Table 1 (below):

TABLE 1

Inhibitor Functionality	Hereafter referred to as
VSA homopolymer	Inhibitor A
diethylene triamine pentakis(methylene phosphonic acid), 45% aqueous solution of sodium salt	Inhibitor B
phosphonate end-capped poly(acrylic acid)	Inhibitor C
phosphonate end-capped VSA/AA copolymer	Inhibitor D
VPA/VSA random copolymer	Inhibitor E
AA/MAA/VSA random copolymer	Inhibitor F

Test brines were North Sea seawater and a medium-scaling formation water (Nelson). Brine formulations are given in Table 2 below. Brines were mixed in a 50:50 ratio. All brines were buffered to pH = 5.5 using a sodium acetate/acetic acid buffer (34g of sodium acetate tri-hydrate and 0.75g of concentrated acetic acid, made up to 250ml in a volumetric flask with distilled water). All brines were filtered through a 0.45 μ m filter before use (to remove potential nucleation sites).

TABLE 2
Composition of brines used in
static barium sulphate inhibition efficiency tests

Salt	Seawater g/l	Synthetic Nelson formation water g/l
NaCl	24.41	79.50
CaCl ₂ ·6H ₂ O	2.34	10.93
MgCl ₂ ·6H ₂ O	11.44	6.18
KCl	0.877	1.25
BaCl ₂ ·2H ₂ O	-	0.48
SrCl ₂ ·6H ₂ O	-	2.35
Na ₂ SO ₄	3.98	-

Inhibitor stock solutions of 1000ppm (in seawater) were diluted to give 20ppm, 30ppm and 40ppm stocks in seawater. Two aliquots of 100mls of each stock were placed in two 100ml Azlon® plastic bottles (test in duplicate). Two sets of blanks were also prepared containing seawater (minimum barium blank) and distilled water (maximum barium blank). Into an equivalent number of 250ml Azlon® bottles were placed 100mls of formation water and 2mls of buffer. All seawater bottles were placed in a

refrigerator at 5°C and all formation water bottles were placed in a pre-cooled water bath at 5°C. Bottles were kept for 2 hours at that temperature. The seawater was then added to the formation water and the bottles replaced in the water bath at 5°C. This gave final inhibitor test doses of 5, 10 and 15ppm inhibitor. Bottles were sampled after 2 and 22 hours. These sampling times represent scale inhibition by nucleation inhibition and crystal growth inhibition mechanisms respectively. A 1ml sample was taken from each bottle (taking care not to pick up any deposited scale). This was injected into a plastics test tube containing 9mls of a pre-prepared quench solution (28.559g of KCl, 5g of polyvinylsulphonic acid in distilled water, adjusted to pH + 8.0 – 8.5 with NaOH and made up to 5 litres in a 5 litre volumetric flask). Each sample was analysed for residual barium by ICP analysis.

The barium sulphate inhibition efficiency was then calculated as follows:

$$\% \text{ efficiency} = \frac{[\text{Ba}^{2+} \text{ in sample}] - [\text{Ba}^{2+}]_{\min}}{[\text{Ba}^{2+}]_{\max} - [\text{Ba}^{2+}]_{\min}} \times 100$$

$[\text{Ba}^{2+}]_{\max} = \text{Ba}^{2+} \text{ content of maximum (FW/H}_2\text{O)blank}$

$[\text{Ba}^{2+}]_{\min} = \text{Ba}^{2+} \text{ content of minimum (FW/SW)blank}$

The results are shown in tabular form in Table 3 (below) and in graphical form in the accompanying drawing.

TABLE 3

Inhibitor	% Ba efficiency					
	2 hours			22 hours		
	5ppm	10ppm	15ppm	5ppm	10ppm	15ppm
A	41	53	81	6	14	24
F	33	65	90	11	16	25
B	30	24	16	2	2	1
C	28	69	78	10	19	25
E	65	92	104	15	33	55
D	21	59	77	11	22	39

The results show the enhanced scale inhibiting properties of a copolymer of VPA and VSA in comparison with other sulphonate polymers.

EXAMPLE 2

Mains water (102 ppm Calcium hardness, 136 ppm total hardness, 85 ppm total alkalinity (all expressed as CaCO₃) and pH 8) was adjusted to pH 11 using saturated calcium oxide/hydroxide solution and the efficacy of a selection of inhibitors to control scaling was evaluated over a 24 hour period at dose levels of 10 and 50ppm product.

HACH NTU and soluble calcium measurements were used to determine the efficacy of the inhibitors. The results are summarised in Table 4.

TABLE 4

Product	ppm dosage (as solids)	% Inhibition
Blank	0	0
Phosphonate scale inhibitor*	5	76
Phosphonate scale inhibitor*	25	85
Inhibitor D	2.5	85
Inhibitor D	12.5	100

* (2-hydroxyethyl) iminobis(methylenephosphonic acid)

The results clearly demonstrate the ability of Inhibitor D to control scale deposition at pH 11 under stressed conditions.

Inhibitor D is as referred to in Table 1, a copolymer of acrylic acid and vinylsulphonic acid, with a terminal vinylidine diphosphonic acid group.

CLAIMS

1. The use of a composition in a water system to inhibit the formation of scale at both high (e.g. wellhead) and low (e.g. seabed) temperatures wherein the composition comprises:

(a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) or an unsaturated carboxylic acid (or salt of such an acid);

or

(b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) and an unsaturated carboxylic acid (or salt of such an acid).

2. The use of a composition in a water system operating under highly alkaline conditions to control the deposition of scale wherein the composition comprises:

(a) a copolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) or an unsaturated carboxylic acid (or salt of such an acid)

or

(b) a terpolymer of an unsaturated phosphonic acid (or salt of such an acid) with an unsaturated sulphonic acid (or salt of such an acid) and an unsaturated carboxylic acid (or salt of such an acid).

3. Use according to Claim 1 or Claim 2 wherein the composition comprises a copolymer of vinylphosphonic acid (VPA) (or a salt thereof) and vinylsulphonic acid (VSA) (or a salt thereof).

4. Use according to any preceding claim wherein the composition comprises a 1 : 20 copolymer of VPA and VSA.

5. Use according to Claim 1 or Claim 2 wherein the composition comprises a copolymer of VPA (or a salt thereof) and acrylic acid (AA) (or a salt thereof) or methacrylic acid (MAA) (or a salt thereof).

6. Use according to Claim 1 or Claim 2 wherein the composition comprises a copolymer of vinylidene-1,1-diphosphonic acid (VDPA) (or a salt thereof) and AA (or a salt thereof) or MAA (or a salt thereof).

7. Use according to Claim 1 or Claim 2 wherein the composition comprises a copolymer of VDPA (or a salt thereof) and VSA (or a salt thereof).

8. Use according to Claim 1 or Claim 2 wherein the composition comprises a terpolymer of VPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof).

9. Use according to Claim 1 or Claim 2 wherein the composition comprises a terpolymer of VPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof).

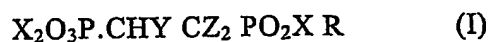
10. Use according to Claim 1 or Claim 2 wherein the composition comprises a terpolymer of VDPA (or a salt thereof), AA (or a salt thereof) and VSA (or a salt thereof).

11. Use according to Claim 1 or Claim 2 wherein the composition comprises a terpolymer of VDPA (or a salt thereof), MAA (or a salt thereof) and VSA (or a salt thereof).

12. Use according to any one of the preceding claims wherein in the composition any salt of the phosphonic acid, sulphonic acid or carboxylic acid is a wholly-neutralised or partially-neutralised salt.

13. Use according to Claim 12, in which the salt is a sodium salt, a potassium salt or an ammonium salt.
14. Use according to any one of Claims 1 and 3 to 13 when dependent on Claim 1 comprising the addition to the water system of a scale inhibiting amount of the composition.
15. Use according to Claim 14, in which the composition is added to the water system in an amount of up to 1000 ppm.
16. Use according to Claim 14 or 15, in which the composition is added to the water system in an amount of from 1 ppm to 200 ppm.
17. Use according to any one of Claims 14 to 16, in which the system water temperature at the wellhead is in the range 80-200°C and the seabed temperature, is below 40 degrees Celcius and typically as low as 5 degrees Celsius.
18. Use according to any one of Claims 2 and 3 to 13 when dependent on Claim 2 comprising the addition to the water system of a scale deposition controlling amount of the composition.
19. A water system treated by the use of a composition according to any one of Claims 14 to 17.
20. A water system according to Claim 19, which is operatively associated with an oilfield or oil-well.
21. A water system treated by use of a composition according to Claim 18.

22. The use in a water system of a composition to control the deposition of scale under highly alkaline conditions wherein the composition has the formula:



where X is H or an alkali metal, alkaline earth or other polyvalent metal, ammonium or an organic base, and R is hydrogen, an alkyl moiety or a group, or polymeric chain comprising between 1 and 100,000 groups, said group or groups being derived from at least one unsaturated compound in which the multiple bond is activated chemically by an adjacent electron withdrawing group, and Y and Z are each hydrogen, a PO_3X_2 , SO_3X or CO_2X group or an alkyl or aryl moiety.

23. Use of a composition according to claim 22 wherein X is H or an alkali metal or ammonia, Y is H, each Z is H, and R is H.

24. Use of a composition according to claim 22 wherein X is H or an alkali metal or ammonia, Y is $\text{X}_2\text{O}_3\text{P}-$, each Z is H and R is H.

25. Use of a composition according to claim 22 wherein X is H or an alkali metal or ammonia, Y is H or $\text{X}_2\text{O}_3\text{P}-$, each Z is H and R is $-\text{CH}_2\text{CHYPO}_3\text{X}_2$.

26. Use of a composition according to claim 22 wherein the compound of formula (I) is a telomer and wherein R is a polymeric or copolymeric group formed from at least one monomer selected from unsaturated sulphonic acids, phosphonic acids, carboxylic acids and their water soluble salts.

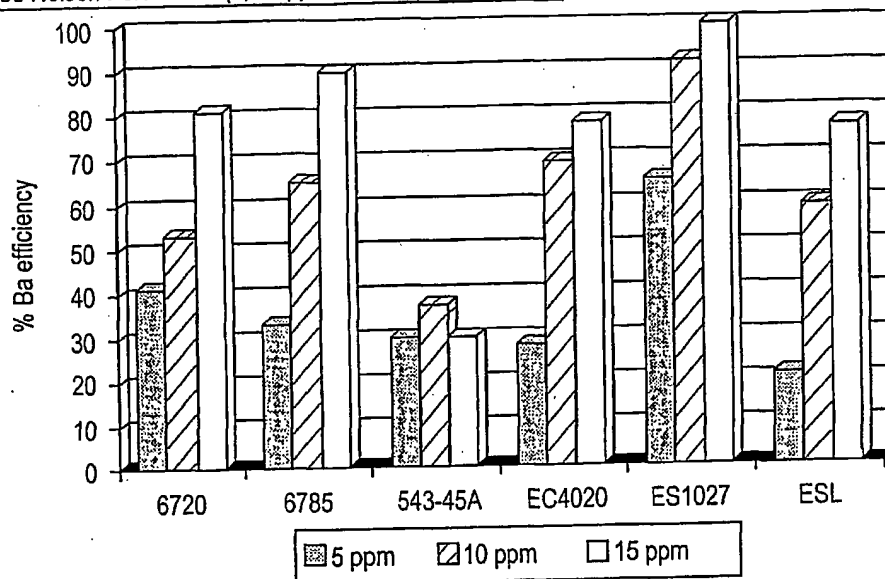
27. Use of a composition according to claim 26 wherein the monomer comprises vinyl sulphonic acid and/or its water soluble salt, vinyl

phosphonic acid and/or its water soluble salts, vinylidene diphosphonic acid and/or its water soluble salts or acrylic acid.

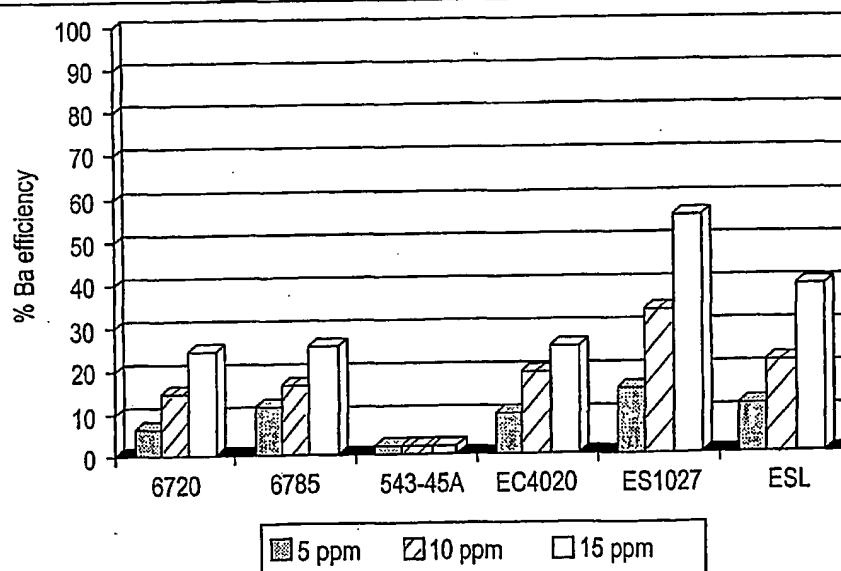
28. Use of a composition according to claim 26 or claim 27 wherein the monomer comprises at least one member selected from methacrylic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, vinyl alcohol, vinyl chloride, vinyl acetate, styrene sulphonic acid, 2-acrylamido-2 methylpropane sulphonic acid and their water soluble salts.

1/1

Barium sulphate inhibition efficiencies after 2hrs

50 Nelson Forties FW (2,000ppm Ca^{2+}) : 50 SW @ 50°C

Barium sulphate inhibition efficiencies after 22hrs

50 Nelson Forties FW (2,000ppm Ca^{2+}) : 50 SW @ 50°C

INTERNATIONAL SEARCH REPORT

International Application No
PC 1/ 032004/003197

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C02F5/14		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 643 081 A (HOECHST AG) 15 March 1995 (1995-03-15) the whole document	1-21
X	EP 0 861 846 A (ALBRIGHT & WILSON UK LTD) 2 September 1998 (1998-09-02) the whole document	22-28
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 29 October 2004		Date of mailing of the international search report 19/11/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer Serra, R

INTERNATIONAL SEARCH REPORT

A summary of patent family members

International Application No

PC 1/ GB2004/003197

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0643081	A	15-03-1995	DE 4330699 A1	16-03-1995
			EP 0643081 A1	15-03-1995
			JP 7173226 A	11-07-1995
			NO 943335 A	13-03-1995
EP 0861846	A	02-09-1998	AT 236175 T	15-04-2003
			AU 727273 B2	07-12-2000
			AU 5627498 A	03-09-1998
			CA 2230517 A1	26-08-1998
			DE 69812753 D1	08-05-2003
			DE 69812753 T2	05-02-2004
			DK 861846 T3	21-07-2003
			EP 0861846 A2	02-09-1998
			ES 2196413 T3	16-12-2003
			GB 2322627 A ,B	02-09-1998
			NO 980782 A	27-08-1998
			US 6071434 A	06-06-2000